

Continuous monitoring of dioxins

Michael J. Coggiola (michael.coggiola@sri.com; 650-859-3045)

Harald Oser (harald.oser@sri.com; 650-859-3311)

Gregory W. Faris (gregory.faris@sri.com; 650-859-4131)

David R. Crosley (david.crosley@sri.com; 650-859-2395)

Molecular Physics Laboratory

SRI International

333 Ravenswood Avenue

Menlo Park, CA 94025

1. Introduction

The need for a continuous emissions monitor for the determination of dioxins and furans at realistic (ppt or sub-ppt) concentrations in real time (minutes) is widely recognized in the waste combustion community. The key issues are overall sensitivity, and selectivity among the many congeners found in real applications. At SRI International we have begun a project designed to meet these needs. Our instrument is based on supersonic jet expansion and cooling, followed by resonantly enhanced multiphoton ionization (REMPI) into a mass spectrometer. This furnishes the dual selectivity of tuned laser absorption and mass analysis. We have made direct measurements of several polychlorinated dioxins and furans using a one-color REMPI scheme, and we have demonstrated a two-color excitation scheme.

2. Objective

Emission control strategies must ultimately rely upon a careful assessment of the link between health effects and ambient, human exposure levels to hazardous air pollutants (HAPs). Because polychlorinated organic compounds in general, and dioxins and furans in particular, are among the most toxic of HAPs, SRI International is developing a continuous emission monitor (CEM) for these species using the jet-REMPI technique under support from DOE. The unique capability for real-time detection and identification of these and other toxic HAPs directly in incinerator emissions using a CEM instrument is an essential component of emissions modeling, dispersion modeling, source apportionment, and ultimately, of human exposure modeling. Jet-REMPI is the only instrumental technique that can provide the speed, breadth, and sensitivity of measurement capabilities that are required in support of the development of a comprehensive strategy to monitor and control emissions of dioxins and furans from waste incinerators.

Our technique will provide real-time dioxin and furan concentrations rather than the multi-hour or multi-day averages as in the case for existing, conventional sampling and analysis methods. This capability will allow a detailed investigation of the relationship between dioxin emissions and the incinerator operating parameters and waste feed characteristics. Such a study may reveal that “puffs” (transient pollutant emission events) account for a majority of the dioxin emissions, and hence only short-term control methods would be required to meet time-averaged regulatory emission limits. Such control strategies may be much more cost effective than full-time emission control approaches. Tailoring the emission control strategy in response to minute-by-minute changes in the emission of hazardous pollutants can only be accomplished if a suitable CEM is available, such as our jet-REMPI based instrument.

3. Approach and Technology Description

Our approach to acquiring the data on dioxin and furan levels is to perform direct measurement of specific congeners using the jet-REMPI method. Jet-REMPI is an ultra-sensitive analytical technique that can selectively identify and quantify vapor-phase constituents present at ppt levels in incinerator emissions without preconcentration or sample collection.

In recent years, many significant improvements have been made in the detection of hazardous, vapor-phase, organic compounds of environmental importance. Several research groups, including SRI, [1-3], DLR, [4], and The Technical University of Munich, Germany, [5], have demonstrated instruments or components of instruments based on REMPI and mass spectrometry.

A schematic of our laboratory prototype dioxin CEM is shown in Figure 1. Ions produced by resonance enhanced multiphoton ionization (REMPI) are typically detected using a time-of-flight mass spectrometer (TOF-MS) that takes advantage of the pulsed nature and well-defined temporal character of laser ionization. The simultaneous detection by mass and wavelength yields extremely high chemical selectivity crucial to identifying one trace compound in the midst of many other similar ones. Typical sensitivities of conventional REMPI TOF-MS systems that do not use sample molecule cooling are in the mg/dscm range and higher, which is totally insufficient either for a laboratory system or for regulatory monitoring of chlorinated aromatics in a waste treatment process such as an incinerator.

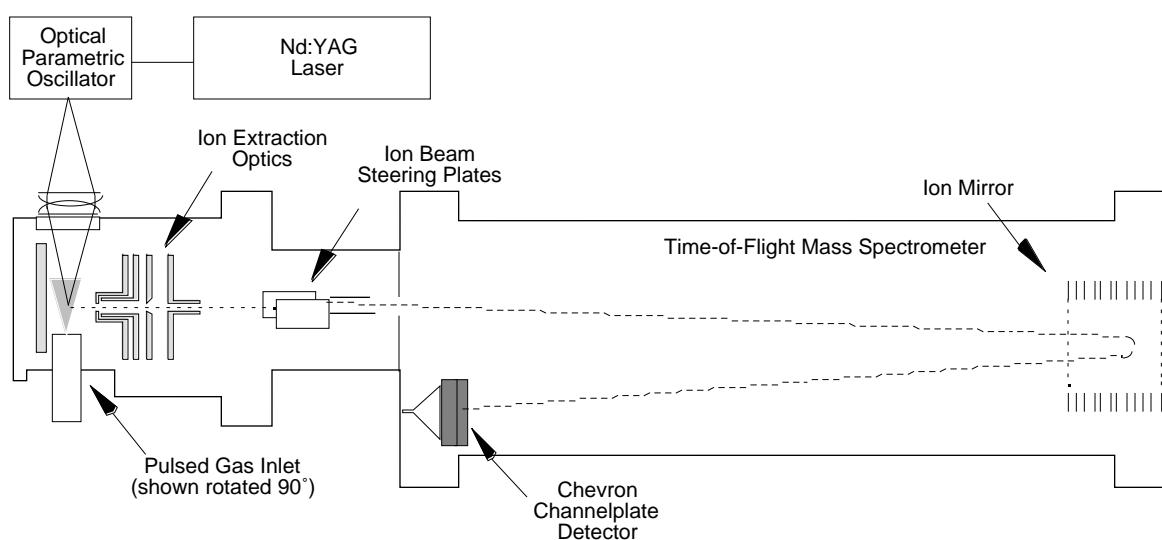


Figure 1. Schematic of the laboratory prototype jet-REMPI apparatus.

A major improvement in sensitivity without loss in selectivity can be achieved using a pulsed gas valve that produces a supersonic expansion. Pulsed gas valves provide a number of advantages over continuous gas inlets, including reduced gas flow and hence smaller vacuum pumps, higher local gas densities, well-defined spatial distribution, significantly reduced translational energy distribution orthogonal to the propagation direction, and reduced internal (vibrational and rotational) temperatures leading to greatly enhanced spectroscopic resolution.

REMPI is a highly sensitive, highly species-selective, gas-phase analysis technique that has been applied to numerous problems in molecular spectroscopy and combustion research. The left side of Figure 2 shows a one-color, two-photon REMPI excitation/ionization scheme. This scheme can be used when the first excited state (S_1) lies more than half way to the ionization

continuum. Resonant absorption of a single photon excites the molecule from the ground state (S_0) to S_1 , where absorption of a second photon of the same wavelength results in ionization. The wavelength specific S_0 to S_1 transition provides the required selectivity among the many closely related dioxin and furan congeners. The two-color, two-photon REMPI scheme is discussed below.

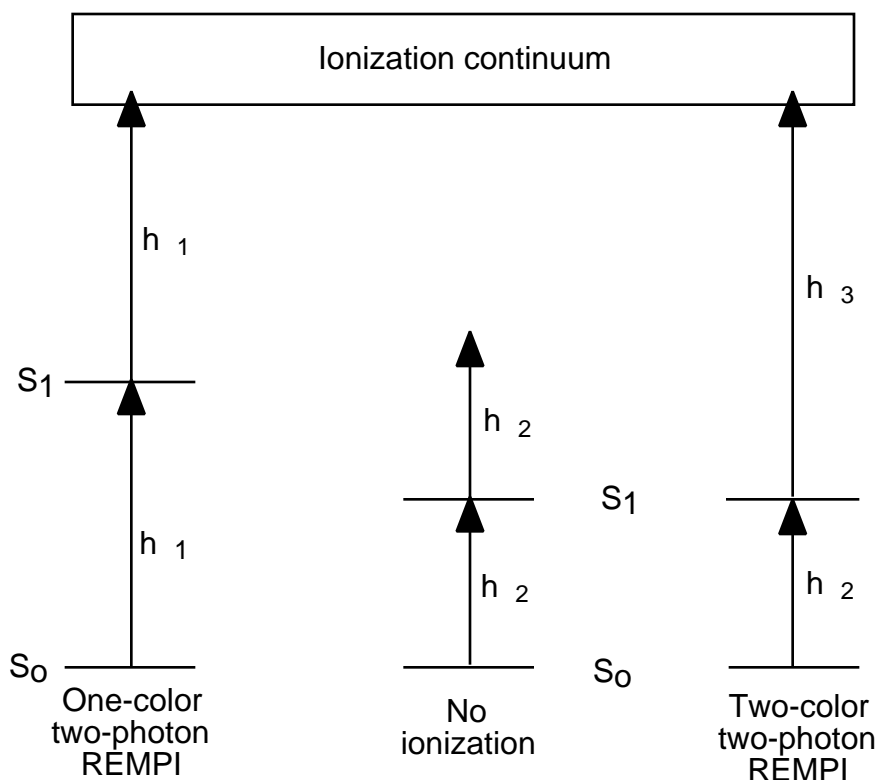


Figure 2. Resonance enhanced multiphoton ionization (REMPI) schemes.

For REMPI of complex molecules, such as dioxins, the spectra can be simplified greatly by expansion through a nozzle. Adiabatic expansion results in low sample temperatures, which increases the electronic ground state population and narrows the resonance line widths through reduction in molecule velocities (reduced Doppler or temperature broadening) and through reduction in transition-perturbing collisions (reduced pressure broadening). These reduced linewidths lessen the ionization of other molecular species (interferences – leading to improved selectivity – and make the peak absorption larger—leading to improved sensitivity. One or more wavelengths are used to ionize the cooled gas molecules by absorption of two or more photons, one of which must be resonant with an electronic transition in the target molecule. Figure 3 shows a typical example of the resonance line narrowing produced by adiabatic expansion as compared with the room temperature absorption spectrum.

Because different isomers of a given chemical composition may have very different toxicities, it is essential that a measurement instrument be capable of distinguishing among isomers. Our instrument is able to do this without any sample pre-separation, such as by gas chromatography, for example, because of the inherent ability of optical spectroscopy (REMPI in

this case) to readily distinguish among isomers. The selectivity of the optical spectroscopy is vastly improved through the pulsed nozzle cooling effects, as discussed above.

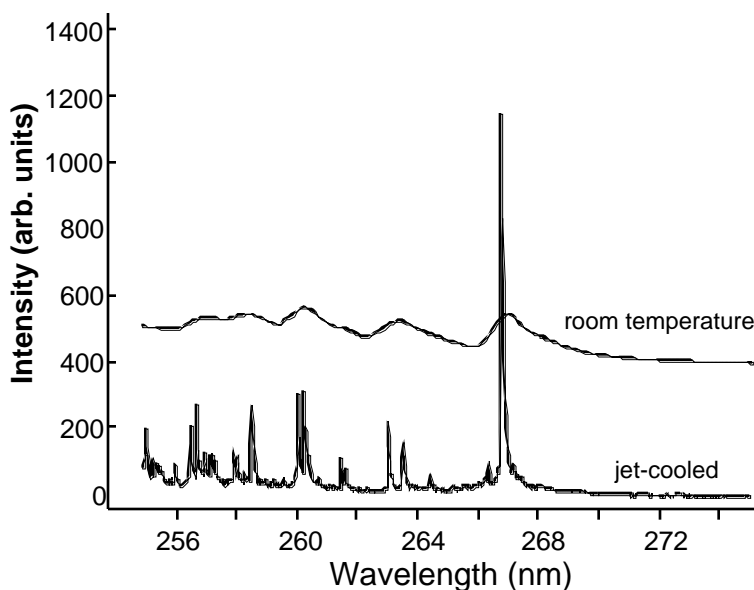


Figure 3. REMPI wavelength dependence for toluene measured in a jet-cooled adiabatic expansion as compared with room temperature absorption. The room temperature data has been multiplied by 20 and shifted vertically.

The mass spectrometric capabilities of our reflectron-type TOF mass analyzer include an upper mass range typically up to 500 amu, limited only by the size of the mass spectral data files, and mass resolution (m/m) greater than 500.

The laser system used in our preliminary experiments described below consists of a Continuum Powerlite Precision 9010 Nd:YAG and Sunlite EX OPO with a nominal tuning range in the visible between 445 and 710 nm, a 5 ns pulse width, and a repetition rate of 10 Hz. Frequency doubling is achieved using an Inrad autotracker II. The optical linewidth of the system is approximately 0.1 cm^{-1} .

The pulsed valve is an unmodified General Valve series 9 unit, with an orifice diameter of 0.5 mm. The nominal opening time was 150 μs , with a 2.5 cm separation between the exit of the valve and the ionization region. With the sample reservoir at atmospheric pressure, the two 250 l/s turbomolecular pumps (Varian Turbo V-250) maintain pressures in the ionization chamber and mass spectrometer regions of 10^{-5} Torr, and 5×10^{-7} Torr, respectively.

4. Results

The ionization conditions used to acquire the data included a pulse energy of approximately 1 mJ in a 1.5 mm diameter laser beam. Ion signals from the R. M. Jordan reflectron TOF-MS were amplified by a Ortec 9306 preamplifier with a gain of 85 and a 1 GHz bandwidth, and recorded by a 500 MHz, Signatec DA500A digitizer.

A sample consisting of a mixture of equal amounts of 2,7-dichlorodibenzodioxin (DCDD) and 2,8-DCDD was used to demonstrate isomer selectivity. To simplify these tests, a

small quantity of the liquid mixture was injected into a stainless steel sample flask on the upstream side of the pulsed valve, and room air was used as a carrier gas. All components in the sample stream were heated to prevent condensation. Figure 4 shows the ion signal recorded at m/z 252, corresponding to the parent ion of both isomers. Several individual absorption features are labeled to show which isomer gave rise to the signal. Assignment of these absorption features was made by measuring the jet-REMPI spectra for each isomer separately.

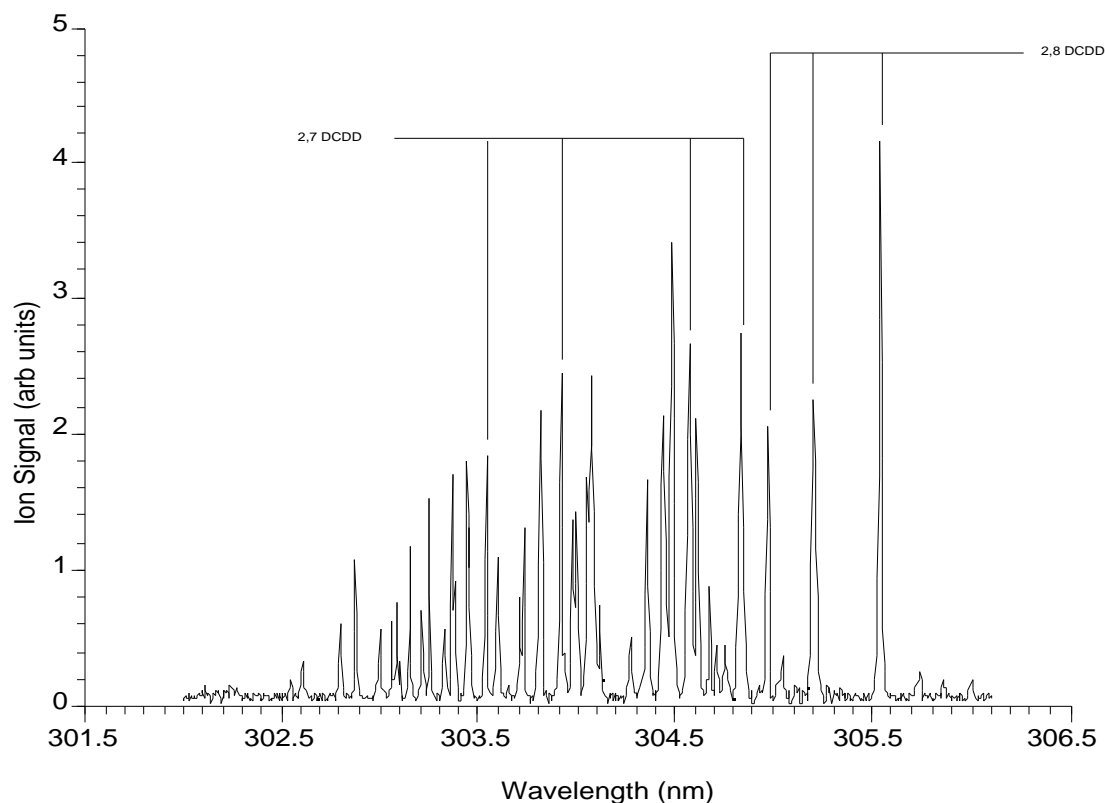


Figure 4. Jet-REMPI wavelength dependence for a equimolar mixture of 2,7-DCDD and 2,8-DCDD measured at m/z 252.

For many molecules of interest, particularly tetrachlorinated and higher dioxins and furans, the one-color, two-photon REMPI excitation and ionization scheme is not possible as the first excited state lies less than half to the ionization limit. This situation is shown in the middle portion of Figure 2. For those molecules, a two-color REMPI scheme must be used where a tunable wavelength is used to excite the first excited state resonantly, and a second, fixed wavelength is used to achieve ionization. The right side of Figure 2 illustrates this REMPI scheme. To demonstrate the two-color approach, we have examined the jet-REMPI wavelength dependence for 1,2-dichlorobenzene. Figure 5 shows the m/z 146 ion signal measured using a combination of tunable uv from the OPO, and 266 nm produced by quadrupling the Nd:YAG fundamental. Since 1,2-dichlorobenzene can be ionized by the one-color, two-photon scheme, we have shown that ion signal in Figure 5 as well. Note that the large absorption peak at 272.61 nm appears using both ionization schemes. However, the absorption peak at 273.58 nm appears only in the two-color signal. This feature arises from the absorption of one photon that is

resonant with vibrationally excited ground state molecules, followed by absorption of a 266 nm photon to produce ionization. Because the absorption of a second photon at 273.58 nm cannot ionize 1,2-dichlorobenzene, this feature does not appear in the one-color REMPI spectrum. As shown in Figure 5, the threshold for the one-color, two-photon process is approximately 273 nm.

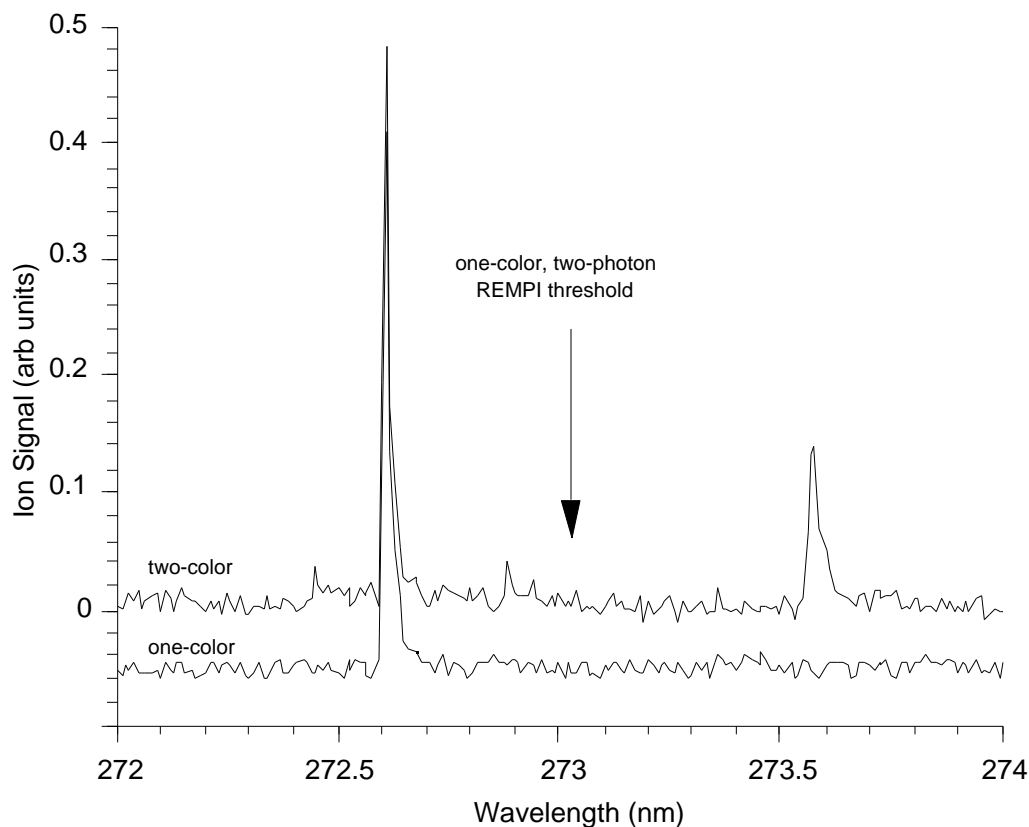


Figure 5. Wavelength dependence of the m/z 146 ion signal for 1,2-dichlorobenzene recorded using both a one-color, two-photon excitation/ionization scheme, and a two-color, two-photon REMPI scheme.

5. Applications

There are at least two different applications for a dioxin CEM in connection with waste incineration. The first would be in support of pollution prevention at the source. For this application, on-line monitoring of suitable precursor compounds would be needed to control dioxin and furan formation and release. The requirements for this application include an instrumental sensitivity in the ppt range, and a thorough knowledge of formation chemistry within the incinerator.

A second application of a dioxin CEM is for compliance monitoring. In this application, on-line monitoring of stack emissions is required to determine the toxic equivalence (TEQ) value. This measurement requires instrumental sensitivity in the ppq range, below the detection limits of any current CEM. Possible approaches to achieve this sensitivity include development of fast

preconcentration techniques and/or the use of indicator substances for the TEQ determination. Surrogate compounds might include chlorobenzenes or lowly chlorinated dioxin and furan congeners. The use of surrogates requires determination of the correlation between the TEQ and the levels of the indicator compounds. This correlation may be strongly dependent on the specifics of the incinerator, its operating conditions, and the feedstock.

6. Future Activities

During the next phase of our development program, we will investigate the spectroscopy of the lowly chlorinated dioxin and furan congeners which contribute to the TEQ. Improvements will be made to the instrument, including new ion optics and an improved pulsed valve design. In addition, issues associated with stack sampling, preconcentration, and particulates will be addressed.

7. Acknowledgements

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8. References

1. E. Y. Xu, T. Tsuboi, R. Kachru, and H. Helm, "Four-photon dissociation and ionization of H₂," *Phys Rev.* **A36**, 5645-5653 (1987).
2. M. Rossi and D. J. Eckstrom, "Quantitative aspects of benzene photoionization at 248 nm," *Chem. Phys. Lett.* **120**, 118-123 (1985).
3. M. Rossi and H. Helm, "Multiphoton ionization of vinylchloride, trifluoroethylene, and benzene at 193 nm," *J. Chem. Phys.* **87**, 902-909 (1987).
4. H. Oser, R. Thanner, H. H. Grotheer, "Jet-REMPI for the detection of trace gas compounds in complex gas mixtures, a tool for kinetic research and incinerator process control," *Comb. Sci. and Tech.* **116**, 567-572 (1996).
5. R. Zimmermann, U. Boesl, D. Lenoir, A. Kettrup, Th. L. Grebner, and H. J. Neusser, "The ionization energies of polychlorinated dibenzo-p-dioxins: new experimental results and theoretical studies," *Int. J. Mass Spectr. and Ion Phys.* **145**, 97-108 (1995).